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FINAL REPORT
FOR THE PROJECT

The Absolute Rates of Some Free Radical Reactions

at the

Chemistry Department
University of Southern California
Los Angeles 7, California

Period Covered: 20 October, 1960-19 October, 1961

AROD Project No.: TB2-001

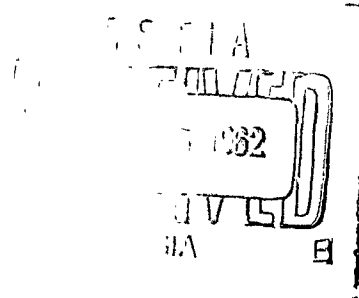
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I. Introduction

The present report terminates a period of support to the author by the Office of Ordnance Research that began as a contract in 1952 and continued without interruption until the present closing date. In its last year this support was changed over from a contract to a grant basis. Much of the work of this period has already been summarized in the form of technical, quarterly and final reports and shall not be repeated here. However it is inevitable that the present report shall overlap the preceding periods and there will be some discussion of the work of the period 1959-1960.

The program in kinetics which has been supported during this time began in 1952 as an exploration into the mechanism of energy transfer in molecules and its effect on the rate of chemical reactions. In its recent years, the bulk of our effort has gone into a study of the quantitative aspects of free radical reactions and the relations between rate constants and molecular structure. The papers which have just been published as well as those still in press or in process of preparation will give the details of this work.

Inevitably, under the conditions of an extended research effort, not all the work has been reported in the open literature nor has all of it even been put in manuscript form. In the present report there will be references to a number of such results which will probably not be prepared for publication before another 6 to 8 months.

In closing the author wishes to express his deep appreciation to the Office of Ordnance Research for the most generous support which has made possible the present research work.

Sidney W. Benson
Professor of Chemistry

Los Angeles, California
January 10, 1962

II. Summary of Results and Publications

1. "On the Existence of Energy Chains in the Ozone Decomposition," by Sidney W. Benson, Jour. Chem. Phys. 33, 939 (1960).

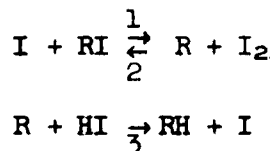
Abstract

A review of the data on O_3 photolysis indicates that excited O atoms (1D) can produce short chains. There is no evidence however to support the hypothesis of an energy chain propagated by vibrationally excited O_2 molecules either in pyrolysis or photolysis.

2. "Kinetics of the Reactions of Alkyl Iodides with HI," by Sidney W. Benson and Edward O'Neal, Jour. Chem. Phys. 34, 514 (1961).

Abstract

A reexamination of Ogg's data on the kinetics of the reactions of $RI + HI \rightarrow RH + I_2$ where $R = CH_3$, C_2H_5 or $n-C_3H_7$, shows that the mechanism is a simple I-atom catalyzed, radical reaction with the steps



The rate expression is

$$d(I_2)/dt = k_1 k_3 K^{1/2} (RI)(HI) / [k_2(I_2) + k_3(HI)] (I_2)^{-1/2}$$

where K is the equilibrium constant for dissociation of I_2 . Values are obtained for k_1 , and the inhibition ratio k_3/k_2 at one temperature and for $k_1 k_3/k_2$ over a temperature range. Using some entropy estimates, values are deduced for A_1 , A_2 , A_3 , and A_4 (reverse of step 3) all of which seem quite reasonable and self-consistent. The difference ($E_3 - E_2$) appears to lie between 0 and 2 kcal/mole while E_1 is in excess of the estimated endothermicity of reaction (1) by

not more than 1.5 kcal/mole. There seems to be good agreement with independent data on the kinetics of pyrolysis of alkyl and aryl iodides which also turn out to be I-atom catalyzed, radical reactions.

3. "Reaction of Cyclopropane with Iodine and Some Observations on the Isomerization of Cyclopropane," by Sidney W. Benson, Jour. Chem. Phys. 34, 521 (1961).

Abstract

The kinetic and thermodynamic data of Ogg and Priest on the system $I_2 + \text{cyclopropane} \rightleftharpoons \text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ are reexamined. Using an entropy for $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$, estimated from additivity rules of 93.0 ± 1.5 eu, and the experimental value of K_{eq} , ΔH° is found to be -17.2 ± 0.9 kcal. This gives $H_f^\circ(\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}) = 10.4$ kcal/mole and the use of group additivity rules allow the values of ΔH_f° for EtI and $n\text{-C}_3\text{H}_7\text{I}$ to be fixed at -2.3 ± 0.5 and -7.3 ± 0.5 kcal/mole, respectively. For CH_3I , $\Delta H_f^\circ = 2.6 \pm 1$ kcal/mole. The kinetic mechanism is also reexamined and from entropy and energy estimates for the free radical species, values of all of the rate constants are evaluated. These are in good agreement with values for similar reactions. It is proposed that the I_2 -catalyzed isomerization of cyclopropane proceeds through the step $I + \text{ICH}_2\text{CH}_2\text{CH}_2\text{I} \rightarrow \text{HI} + \text{ICH}_2\text{-CH=CH}_2 + I$, followed by a rapid, atom-catalyzed reaction of allyl iodide with HI to give propylene. The rate constants for such a step are also in good agreement with those for similar reactions. Extension of the data to cyclopropane-propylene isomerization is made and it is shown that the most reasonable path involves the trimethylene radical as an intermediate. Its lifetime is, however, very short $\sim 10^{-11}$ sec. Slater's model for this reaction is shown

to be implausible. These data indicate an activation energy for the cyclization of the trimethylene free radical of about 8 kcal. This is reasonable only if the end CH_2 groups in trimethylene are interacting via a "bent" bond. In such case the activation energy arises from the necessity for eclipsed configurations. A similar analysis is made for cyclobutane and the tetramethylene radical with compatible results. For cyclopropane the strain energy is 30 kcal and for cyclobutane 28 kcal.

4. "The Pyrolysis of Di-Tertiary Butyl Peroxide. Temperature Gradients and Chain Contribution to the Rate," by Leslie Batt and Sidney W. Benson, Jour. Chem. Phys. 36 (in press, expected Feb.) (1962).

Abstract

An investigation of the pyrolysis of di-tertiary butyl peroxide over the range 27-130 mm Hg pressure and 130-160°C has shown that the experimental stoichiometry is 3.0 rather than the previously reported 2.9. Trace amounts of $t\text{-BuOH}$ (0.5 to 1.0%), isobutylene oxide (1-2%) and $t\text{-BuOMe}$ (0.02%) have been identified as well as biacetonyl and small amounts of other ketones. Using spherical vessels and octopus vessels of large surface/volume ratio it is shown that the previously reported scatter in the Arrhenius parameters can be attributed to temperature gradients established in the vessel. This is confirmed by direct measurement of the gas temperature with fine thermocouple wires in thin glass wells.

The best rate constant for the first order decomposition in the absence of temperature gradients is given by:
 $\log k = 15.6 - 37,400/4.575T \text{ sec}^{-1}$ with an uncertainty in E of about ± 0.5 kcal. Assuming zero activation energy for

the recombination of t-butoxy radicals, this gives the peroxide bond dissociation energy of 37.4 ± 0.5 kcal/mole. An estimate of the standard entropy change for $\text{dtBP} \rightarrow 2 \text{ t-BuO}$ gives the remarkably low value of $10^{8.2}$ l/m-s for the Arrhenius factor for the recombination of t-BuO radicals. It is shown that such a low value is needed to explain the concordance in Arrhenius parameters for liquid and gas state pyrolyses.

The isobutylene oxide puts a limit to the chain contribution of about 1 to 2%. The t-BuOH and t-BuOMe yields permit independent estimates of the rate of dissociation of t-BuO radicals in fair agreement with each other and other investigations.

The explosion limits for the decomposition are estimated to be about 7.5 atmospheres (150°C). The present work confirms the importance of temperature gradients in contributing to spurious activation energies for very exothermic reactions.

5. "Photolysis of Acetone in the Presence of HI. The Kinetics of Decomposition of the CH_3CO Radical," by Edward O'Neal and Sidney W. Benson, Jour. Chem. Phys. (accepted for publication, Dec. 1961).

Abstract

Acetone over a range of pressures and temperatures ($1.2 - 15$ cm Hg; $126-295^\circ\text{C}$) was photolyzed with light of 3130 \AA in the presence of small amounts of hydrogen iodide. The primary process was found to be the C-C split to form acetyl and methyl radicals. Hydrogen iodide acted as an excellent radical "trap" for these radicals. No spontaneous decomposition of acetyl radicals was observed. Relative rates of methyl radical reactions with iodine and hydrogen iodide were measured. Complications due to surface effects in these reactions are considered.

Kinetic constants for the reactions $\text{CH}_3 + \text{HI} \rightarrow \text{CH}_4 + \text{I}$ (1); $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$ (2) are $E_1 - E_2 = 1.3 \pm 0.5$ kcal, $A_2/A_1 = 2.4$, and $\log (k_1/k_2) = -0.38 - 1,300/4.575T$.

Above 200°C the acetyl radical decomposition is measurable and the rate constant is observed to be pressure dependent. The pressure dependence is treated by an approximate method related to the Hinshelwood-Lindemann equation and the high and low pressure limiting rate constants are given by: $\log k = 10.3 - 15,000/4.575T \text{ sec}^{-1}$, $\log k_0 = 11.5 - 12,000/4.575T \text{ (1/mole-sec)}$. The number of vibrational modes S , contributing to the decomposition is 4.5 and the life time of the excited acetyl radical is $t = 10^{-8}$ sec. The abnormally low frequency factor of the high pressure rate constant implies a non-adiabatic decomposition of the acetyl radical. From the kinetic constants, the heat of formation of the acetyl radical is found to be $\Delta H_f^\circ (\text{CH}_3\text{CO}) = -5.6$ kcal and the values of the appropriate bond dissociation energies in a series of acetyl derivatives are tabulated.

6. "Termination Products in the Pyrolysis of Dimethyl Ether," by Kenneth Anderson and Sidney W. Benson, Jour. Chem. Phys. (accepted for publication, Dec. 1961).

Abstract

Termination processes in the pyrolysis of dimethyl ether studied by trace product analysis using gas-liquid chromatography revealed the presence of methyl ethyl ether, 1,2-dimethoxyethane and methanol. These ethers had been predicted in the work of Benson and Jain by including CH_3OCH_2 as a chain terminator and their identification is evidence for the reaction $\text{CH}_3\text{OCH}_2 \rightarrow \text{CH}_3 + \text{CH}_2\text{O}$ being an energy transfer process in its second order region. Methanol was also predicted from the reactions of CH_3O or

CH₂OH. Quantitative measurement of the trace termination products were made to obtain yields for MeOEt, Me₂O and C₂H₆ which could be used to calculate the rate constant ratio, k_2'/k_2 for the attack by CH₃ on MeOEt compared to Me₂O. When the steady state is approached from both sides k_2'/k_2 ranges from 4-12 and is greater than unity as expected. A reasonable difference in activation energy of about 2-4 kcal is estimated for these reactions. However, the MeOEt gas chromatography peak was broad when resolved from Me₂O resulting in loss of precision and together with the required estimates in the steady state equation (7) severely limit the usefulness of trace termination product analysis in determining new rate constants. Ethane was measured and compared to a calculated steady state value. Because of attack on the ethane and the disappearance of radicals by other termination processes the ratio of the Me₂O decomposed to the C₂H₆ found is not as good a measure of the chain length as those calculated from the rate law.

7. "Kinetics of the Reaction of Acetyl Iodide with HI and the I₂-Induced Decomposition of CH₃CHO," by Sidney W. Benson and Edward O'Neal. This paper is in process of preparation and will be submitted to Jour. Chem. Phys. in the near future.

Abstract

The homogeneous reaction of CH₃COI + HI at 160°C yields CH₃CHO + I₂ by a chain mechanism similar to that discovered for the alkyl iodides. At 350°C an I₂-induced decomposition of CH₃CHO leads to CH₄ + CO. All of the quantitative kinetics are in excellent agreement with the CH₃COI + HI reaction as well as that found in the photolysis of CH₃COCH₃ in HI.

8. "HCl-Catalyzed Pyrolysis of Ditertiary Butyl Peroxide," by Sidney W. Benson, Leslie Batt and Michael C. Flowers. This paper is in process of preparation and will be submitted to Jour. Chem. Phys. within the near future.

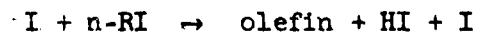
Abstract

From 80°C to 140°C HCl acts as a homogeneous catalyst for the pyrolysis of dtBP. The products are tBuOH + iso-butene oxide (iBuO) as well as CH₄ + acetone + iBuO. The rate is independent of (HCl) and inversely proportional to (acetone) which acts as an inhibitor. A complete, quantitative mechanism is obtained from the data. From it one deduces that the reaction Me₃CO → Me₂CO + Me is dependent on the pressure of inert gases. In addition the rate constant for Me + HCl → CH₄ + Cl can be obtained. Small amounts of C₂H₆ are observed which can be accounted for quantitatively but not by the usual techniques.

9. "The Pyrolysis of Organic Iodides," by Sidney W. Benson. This paper has been in preparation over the past few months and will soon be submitted for publication to Jour. Chem. Phys.

Abstract

It is shown that normal alkyl iodides decompose by a rate determining step which is:



and must involve a concerted reaction of H-atom abstraction and double bond formation. Quite possibly the intermediate product is HI₂. The reaction is unique to I atom attack since alkyl iodides do not show an abnormally fast reaction with alkyl radicals or abnormal olefin formation. Secondary

and tertiary iodides including CH_3COI decompose by a slow HI elimination step to produce olefin + HI. The HI thus formed reacts with residual RI to form RH + I_2 . The data for n-PrI, sec-PrI, n-BuI, sec-BuI, iso-BuI, t-BuI, $\text{ICH}_2\text{CH}_2\text{I}$, CH_3COI , $\text{C}_2\text{H}_5\text{I}$, allyl-I, $\phi\text{CH}_2\text{I}$ and $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ are analyzed in detail.

III. List of Scientific Personnel Employed

1. Dr. Edward O'Neal (Post-Doctorate Research Fellow, Feb. 1959 - Aug. 1961).

The present employment has made it possible for Dr. O'Neal to change his field of research to free radical kinetics. He is now teaching and doing research at San Diego State College.

2. Mr. Kenneth Anderson (Candidate for Ph.D. degree; Research Assistant, 1957-1961).

Mr. Anderson has completed all of his Ph.D. requirements except the thesis and will go into college teaching sometime next Fall (1962).

3. Dr. Leslie Batt (Post-Doctorate Research Fellow, Sept. 1959 - Sept. 1961).

Dr. Batt has now returned to England where he has a research appointment with Dr. Norrish's group at Cambridge University.